Insertion of Dimethyl Acetylenedicarboxylate into α,ω-Dodecatrienediylnickel

By RAYMOND BAKER*, PETER BEVAN, and RICHARD C. COOKSON*
(*Department of Chemistry, The University, Southampton* SO9 5NH)

Summary The reaction of dimethyl acetylenedicarboxylate with α,ω-dodecatrienediylnickel at 0 °C yields approximately equal amounts of twelve- and fourteen-membered ring products, whereas, at −78 °C, 80% of the product has the larger ring; subsequent reactions yielded a series of musk compounds with differing odours.

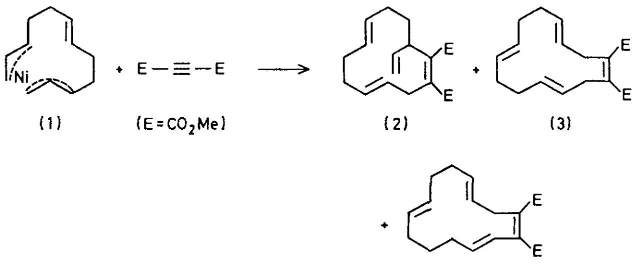
THE nickel complex-catalysed co-oligomerisation of butadiene and substituted alkynes is a useful route to 1,2-disubstituted cyclodecatrienes.[1,2] We now report the formation of 12- and 14-membered rings by the insertion of dimethyl acetylenedicarboxylate into α,ω-dodecatrienediylnickel (**1**).[3]

When 1 mol. equiv. of the diester was added to an ethereal solution of the complex (**1**) [prepared from butadiene and bis(cyclo-octadienyl)nickel[4]] at −78 °C, the deep red solution quickly darkened to a brown-red. After passage of CO, nickel was removed as nickel carbonyl, and the product was separated by column chromatography (silica, 100—120 mesh); light petroleum–Et_2O (10:1) eluted the three diester insertion products (**2**)—(**4**) [30—40% isolated yield based on (**1**)].† At low temperatures (−78 °C) (**3**) and (**4**) constituted about 80% of the product, while at 0 °C the 12-membered ring compound (**2**) and 14-membered ring compounds (**3**) and (**4**) were formed in approximately equal amounts. At longer reaction times, or when a higher ratio of the diester to (**1**) was employed, small amounts of a 14-membered ring compound (**5**) were obtained, corresponding to insertion of two diester molecules. The analogous 16-membered ring compound did not appear to be formed.

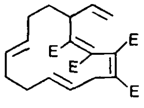
Methyl propiolate also inserted into (**1**) at −78 °C to give a single product (**8**) (20%). The presence of an electron-withdrawing group on the acetylene appears to be essential, since no products were obtained from the attempted reactions of acetylene or methylacetylene.

The mixture of diesters (**3**) and (**4**) was hydrogenated using either nickel P2[5] or 10% palladium on charcoal. In both cases the tetrasubstituted double bond was largely retained. Crystals of pure (**7**), m.p. 78—79 °C, separated from a solution of the hydrogenated esters [(**6**) and (**7**)] in light petroleum.

Reduction at −20 °C of the compound (**7**) with $LiAlH_4$ moderated by 1 mol. equiv. of ethanol[6] gave the diol (**9**). Use of $LiAlH_4$ itself at 0 °C gave approximately equal amounts of (**9**) and the corresponding saturated diol. Reaction of (**9**) with toluene-*p*-sulphonyl chloride and pyridine gave the ether (**10**), which, on hydrogenation with 10% palladium on charcoal, yielded the saturated ether (**11**) together with a small amount of the *trans*-isomer (**12**). The inverse addition of ethanol-moderated $LiAlH_4$ to (**7**) at −20 °C gave the lactone (**13**) (60%). A feature of the compounds (**10**)—(**13**) is their musky odour; whilst (**11**) is a woody musk, (**10**), (**12**), and (**13**) are sweeter.



(1) (E = CO_2Me) (2) (3) (4)



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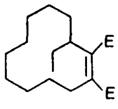

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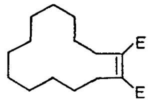

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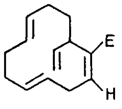

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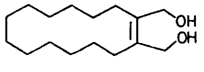

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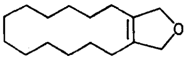

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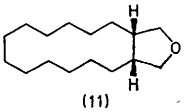

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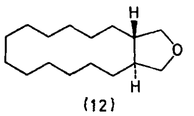

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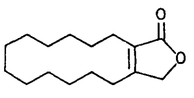

(13)

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† Structure assignments are consistent with spectroscopic properties. The disubstituted double bonds were assigned *trans* on the basis of ν_{max} 965 cm^{-1} for (**2**), (**3**), and (**4**). The tetrasubstituted double bond must result from *cis*-insertion and this is confirmed by subsequent conversion of (**7**) into (**9**)—(**13**).

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